I. THE RADIOACTIVE INDICATOR METHOD APPLIED TO THE LEAD STORAGE CELL

II. A STUDY OF POLYMORPHOUS TRANSITIONS IN LEAD OXIDES

BY

ROBERT ROWAN, JR.

B.S., West Texas State Teachers College, 1934

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1940

URBANA, ILLINOIS
1940

I. THE RADIOACTIVE INDICATOR METHOD APPLIED TO THE LEAD STORAGE CELL

II. A STUDY OF POLYMORPHOUS TRANSITIONS IN LEAD OXIDES

BY

ROBERT ROWAN, JR.

B.S., West Texas State Teachers College, 1934

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1940

URBANA, ILLINOIS
1940

ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor George L. Clark, under whose direction and guidance this research was carried out, for his many suggestions and encouragement throughout the course of the work. He also feels greatly indebted to Dr. J. N. Mrgudich and Dr. S. T. Gross for many valuable suggestions and for the interest they have shown in this investigation.

I. THE RADIOACTIVE INDICATOR METHOD APPLIED TO THE LEAD STORAGE CELL

Many and varied theories have been offered concerning the mechanism of operation of the lead storage cell, and, although the "double sulfate" hypothesis of Gladstone and Tribe with respect to the over-all reaction has been accepted on the basis of abundant experimental evidence, the mechanism at the positive plate is still much debated. It is certain that the question of the migration of lead ions through the electrolyte should be settled as a basis for future research and deduction leading to a true explanation.

The radioactive indicator method was adapted to the problem, using thorium B, a radioactive lead isotope, as a "tagged" lead atom. A number of experiments were performed in which Th-B was placed on the positive or negative plate and the radioactivity of cell parts measured at intervals during the cycling of the cell with a Geiger-Mueller counter. The following results were obtained:

1. No migration of lead ions was detected, either from positive to negative, from negative to positive, or from one part of a plate to another part of the same plate through the electrolyte.

2. The above conclusion is in accord with the theory of double sulfation, and, although not a complete negation of, it is unfavorable to the LeBlanc theory which states, that the positive plate reaction takes place with the formation of plumbic ions as an intermediate product.

II. A STUDY OF POLYMORPHOUS TRANSITIONS IN LEAD OXIDES

This part of the investigation was undertaken for the purpose of making, if possible, contributions to the total knowlege concerning the lead oxides and for the purpose of correlating certain known facts in order to form a clearer picture of the complex lead-oxygen system. Solutions to many of the unsolved problems concerning the lead storage battery can be expected only when investigators are armed with a much more complete knowledge of the phase relationships between the lead oxides.

In 1932, LeBlanc and Eberius found that considerable amounts of oxygen can be added to PbO (up to $PbO_{1.15}$) and subtracted from PbO_2

(down to $PbO_{1.66}$) without a lattice change and that a new, previously undiscovered phase is formed upon further addition or subtraction. This they called "black Pb_3O_4." They also determined that the new lattice can absorb or evolve oxygen without a change between the limits $PbO_{1.15}$ and $PbO_{1.70}$. In 1937 Clark, Schieltz, and Quirke prepared Pb_5O_8 and Pb_2O_3 in macro-crystalline form by a bomb method. Since no report has been made in the literature concerning the relationship between "black Pb_3O_4" and the Pb_5O_8 and Pb_2O_3 of Clark, Schieltz and Quirke, these compounds were prepared so that they could be further studied. For the latter two compounds, the originally described bomb technique was used. To prepare "black Pb_3O_4" a furnace was devised and constructed in which samples could be treated at any constant temperature up to 700°C, either in vacuo or in any atmosphere. Active oxygen determinations were made on most of the samples prepared and X-ray patterns were registered for all.

"Distortion" in red PbO, as in certain other metallic oxides, manifests itself in an increased lattice energy content, an increased catalytic activity, and, on the X-ray pattern, diffuseness of certain lines and a general decrease in intensity of high order interferences. Clark and Tyler first studied distorted PbO with respect to its preparation by decomposition methods, heat of solution, catalytic activity, and X-ray properties. They suggested that the results observed are due to localized, incompletely crystallized surface areas. No work has been done on the distorted red PbO obtained when yellow PbO is subjected to pressure or abbrasion. Thus it was considered desirable to make a quantitative study in an attempt to correlate extent of grinding with degree of distortion, using the rate of decomposition of H_2O_2 as a measure of catalytic activity.

Various miscellaneous experiments, other than the above, were performed. The following results were obtained:

1. In general, increased grinding produces an increase in distortion. The activity of distorted samples prepared by grinding is, in general, about the same as that produced by other methods.

2. It has been shown that distortion in PbO cannot be attributed to an excess of active oxygen in the lattice.

3. Distorted PbO has been obtained in macro-crystalline form by a wet method.

4. Distortion in PbO can be relieved completely by annealing. This fact lends further support to the suggestion of Clark and Tyler that the properties observed must be due to imperfectly crystallized areas. The results, however, do not necessarily imply that these areas reside only in the surface of the particles, as supposed by Clark and Tyler. In fact, the complete and homogeneous reaction of oxygen with distorted PbO, a reaction different from that of normal PbO with oxygen, strongly suggests that the distortion is not a surface phenomenon.

5. The "black red lead" of LeBlanc and Eberius is in reality a mixture of Pb_5O_8 and a new, previously undistinguished phase which we have called PbO_x. Pb_2O_3 does not enter this system.

6. Interplanar spacings have been tabulated for the new phase, although a crystal system or unit cell determination is not possible without supplementary data.

7. The product obtained from the absorption of oxygen near 390°C (the transition temperature for $Pb_5O_8 \rightarrow Pb_3O_4$) by normal PbO was almost pure PbO_x. With distorted PbO, the product was pure Pb_5O_8.

8. Distorted PbO absorbs oxygen much faster than normal PbO. The rate of oxygen absorption is suggested as a measure of distortion in place of the rather unreliable decomposition of H_2O_2 method.

9. A tentative unit cell size determination has been made on Pb_5O_8 from the analysis of a powder pattern. According to this, Pb_5O_8 is tetragonal, $a = 5.508$, $c = 5.460$ A. U., and there is one molecule per unit cell. An unsuccessful attempt was made to prepare crystals large enough for Laue and rotation patterns.

10. Sulfamic acid extraction lowers the active oxygen content of PbO_2 in proportion to the length of treatment.

11. Black PbO, which has been reported by several investigators, was prepared and subjected to X-ray examination. The black color is apparently a surface phenomenon, as claimed by Appleby, since no lattice could be detected except that of the expected yellow PbO.

BIBLIOGRAPHY

1. Paneth, F., Radio-Elements as Indicators, McGraw Hill Book Co., New York, 1928.

2. Vinal, G. W., Storage Batteries, John Wiley & Sons, Inc., New York, 1930

3. Féry, C., Bull. Soc. Chem. *51,* 1019 (1932).

4. Jumau, L., Chemie et Industrie, Spec. No., 689 (Apr. 1934).

5. Seith, W., Z. Elektrochem. *34,* 362 (1928).

6. Thompson, M. K., Trans. Elektrochem. Soc. 75, 4 pp. (preprint) (1939).

7. Fricke R., and Hüttig, G. F. Handbuch der Allgemeinen Chemie, Bd. IX, Hydroxyde und Oxyhydrate, Akademische Verlagsgesellschaft, M. b. H., Leipzig, 1937.

8. Appleby, M. P. and Powell, H. M., J. Chem. Soc. (1931), 2821.

9. Clark, G. L., Scheiltz, N. C. and Quirke, T. T., J. Am. Chem. Soc. *59,* 2305 (1937).

10. Clark, G. L. and Tyler, W. P., J. Am. Chem. Soc. *61,* 58 (1939).

11. Darbyshire, J. A., J. Am. Chem. Soc. (1932), 211.

12. Le Blanc, M. and Eberius, E., Z. physik. Chem. *A160,* 69 (1932).

VITA

The author was born August 20, 1914, in Waco, Texas. He received his elementary and secondary education in various public schools in Texas and New Mexico and was graduated in 1930 from the West Texas State Teachers College Preparatory School at Canyon, Texas. He entered the West Texas State Teachers College at Canyon the same year and was graduated with the degree of Bachelor of Science in chemistry in 1934.

After two years of employment in the chemical industry, he entered the Graduate School of the University of Illinois, where he held a teaching assistantship for the school years 1936-1937, 1937-1938, and 1939-1940. He was a University Fellow during the year 1938-1939.

He is a member of the following societies and fraternities: Alpha Chi Sigma, Alpha Chi, Phi Lambda Upsilon, and Sigma Xi.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549820_0140